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Highlights from recent literature

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Each issue of *Gold Bulletin* contains key highlights from the research and patent literature. Authors who publish high quality work in other journals are invited to send a copy of their publication to the Editor for inclusion in the next issue.

NANOTECHNOLOGY

Gold nanostar substrates for SERS sensing in the femtomolar regime

This invention from the Fabris lab at Rutgers University (WO2015160923 (A1)) relates to Raman spectroscopy-based sensing technique. More particularly, the invention relates to a surface enhanced Raman spectroscopy (SERS) composite and methods of its use and fabrication

Structural isomserism in gold nanoparticles revealed by X-ray crystallography

Revealing structural isomerism in nanoparticles using single-crystal X-ray crystallography remains a largely unresolved task, although it has been theoretically predicted with some experimental clues. Here Chinese and US-based teams report a pair of structural isomers, Au_{38T} and Au_{38Q}, as evidenced using electrospray ionization mass spectrometry, X-ray photoelectron spectroscopy, thermogravimetric analysis and indisputable single-crystal X-ray crystallography (Tian et al., Nature Communications , 6, Article number: 8667 10.1038/ncomms9667). The two isomers show different optical and catalytic properties, and differences in stability. In addition, the less stable Au_{38T} can be irreversibly transformed to the more stable Au_{38Q} at 50 °C in toluene. This work may represent an important advance in revealing structural isomerism at the nanoscale

Sensor Technology for Diagnosing Tuberculosis

A sensor technology comprising a single nano-material (gold nanoparticles and/or carbon nanotube) based sensor or a plurality of sensors in conjunction with a pattern recognition algorithm for non-invasive and accurate diagnosis of tuberculosis caused by M. tuberculosis bacteria in a subject is described by Israeli researchers (US2015301021 (A1)). The sensor technology is suitable for population screening of tuberculosis, particularly in resource-poor and developing countries

Theranostic potential of gold nanoparticle-protein agglomerates

Owing to the ever-increasing applications, glittered with astonishing success of gold nanoparticles (Au NPs) in biomedical research as diagnostic and therapeutic agents, the study of Au NP–protein interaction seems critical for maximizing their theranostic efficiency, and thus demands comprehensive understanding. The mutual interaction of Au NPs and proteins at physiological conditions may result in the aggregation of protein, which can ultimately lead to the formation of Au NP–protein agglomerates. In the present article, researchers from the Indian Institute of Technology (Sanpui et al., Nanoscale, 2015,7, 18411-18423. DOI: 10.1039/C5NR05805H) try to appreciate the plausible steps involved in the Au NP-induced aggregation of proteins and also the importance of the proteins' three-dimensional structures in the process. The Au NP–protein agglomerates can potentially be exploited for efficient loading and subsequent release of various therapeutically important molecules, including anticancer drugs, with the unique opportunity of incorporating hydrophilic as well as hydrophobic drugs in the same nanocarrier system. Moreover, the Au NP–protein agglomerates can act as 'self-diagnostic' systems, allowing investigation of the conformational state of

the associated protein(s) as well as the protein–protein or protein–Au NP interaction within the agglomerates. Furthermore, the potential of these Au NP–protein agglomerates as a novel platform for multifunctional theranostic application along with exciting future-possibilities is highlighted here

Device and method to control release of compound

An implantable time-release delivery system is disclosed, comprising at least one nano-complex of a plurality of vertically aligned rods fixed at one end to a substrate and configured to be implantable within a body, the plurality of vertically aligned rods comprising polypyrrole, gold nanoparticles, and a compound. An electromagnetic field generating device configured to generate an electromagnetic field, positioned in a near field arrangement with respect to the nano-complex, the electromagnetic field causes release of the compound from the nano-complex into the body (WO2015153522 (A1)).

Comparative effect of gold nanorods and nanocages for prostate tumor hyperthermia

Gold nanoparticles have been investigated as photothermal agents, drug delivery carriers, diagnostics, and theranostics (Robinson et al., Journal of Controlled Release, Volume 220, Part A, 28 December 2015, Pages 245–252). As long-term accumulation of nanoparticles in nontarget tissues is a growing concern, it is vital to establish biodistribution profiles, tumor uptake, and tissue residence times for each nano-based system. This study aimed to investigate the prostate tumor uptake, photothermal therapy mediated macromolecular delivery, acute and chronic biodistribution profiles, and organ residence time differences between two nanoparticles, i.e., gold nanocages and gold nanorods. These particles have tunable surface plasmon resonances in the near infrared, but dissimilar shapes. Gold nanocages and nanorods had very different light to heat transduction efficiencies, with gold nanocages requiring 18.4 times fewer particles and approximately half the gold mass of gold nanorods to achieve the same heating profile given a constant laser intensity. It was also observed that while the photothermal macromolecular delivery enhancements were similar for the two systems when dosed by optical density, the tumoral uptake and biodistribution profiles for each of these shapes differed, with the nanocages residing in the liver, kidneys and spleen for less time than the nanorods. Additionally, it was observed that the nanocages were excreted from the body at a higher percentage of injected dose than the nanorods at both the 7 and 28 day time points. These findings have implications for the use of these constructs in diagnostic and therapeutic applications.

Paper-Based Analytical Devices Relying on Visible-Light-Enhanced Glucose/Air Biofuel Cells

A strategy that combines visible-light-enhanced biofuel cells (BFCs) and electrochemical immunosensor into paper-based analytical devices was proposed for sensitive detection of the carbohydrate antigen 15-3 (CA15-3) by Chinese researchers (Wu et al., ACS Appl. Mater. Interfaces, 2015, 7 (43), pp 24330–24337. DOI: 10.1021/acsami.5b07698. The gold nanoparticle modified paper electrode with large surface area and good conductibility was applied as an effective matrix for primary antibodies. The glucose dehydrogenase (GDH) modified gold–silver bimetallic nanoparticles were used as bioanodic biocatalyst and signal magnification label. Poly(terthiophene) (pTTh), a photoresponsive conducting polymer, served as catalyst in cathode for the reduction of oxygen upon illumination by visible light. In the bioanode, electrons were generated through the oxidation of glucose catalyzed by GDH. The amount of electrons is determined by the amount of GDH, which finally depended on the amount of CA15-3. In the cathode, electrons from the bioanode could combine with the generated holes in the HOMO energy level of cathode catalysts pTTh. Meanwhile, the high energy level photoexcited electrons were generated in the LUMO energy level and involved in the oxygen reduction reaction, finally resulting in an increasing current and a decreasing overpotential. According to the current signal, simple and efficient detection of CA15-3 was achieved.

Improving Efficiency of Multicrystalline Silicon and CIGS Solar Cells by Incorporating Metal Nanoparticles

This work studies the use of gold (Au) and silver (Ag) nanoparticles in multicrystalline silicon (mc-Si) and copper-indium-gallium-diselenide (CIGS) solar cells (Jeng et al., Materials 2015, 8(10), 6761-6771; doi:10.3390/ma8105337). Au and Ag nanoparticles are deposited by spin-coating method, which is a simple and low cost process. The random distribution of nanoparticles by spin coating broadens the resonance wavelength of the transmittance. This broadening favors solar cell applications. Metal shadowing competes with light scattering in a manner that varies with nanoparticle concentration. Experimental results reveal that the mc-Si solar cells that incorporate Au nanoparticles outperform those with Ag nanoparticles. The incorporation of suitable concentration of Au and Ag nanoparticles into mc-Si solar cells increases their efficiency enhancement by 5.6% and 4.8%, respectively. Incorporating Au and Ag nanoparticles into CIGS solar cells improve their efficiency enhancement by 1.2% and 1.4%, respectively. The enhancement of the photocurrent in mc-Si solar cells is lower than that in CIGS solar cells, owing to their

different light scattering behaviors and material absorption coefficients

ELECTRONICS

Electroplated solder with eutectic chemical composition

The chip package presented by American researchers at Oracle (US2015318254 (A1)) includes a substrate having a gold (or tin) layer disposed on a surface of the substrate. The gold (or tin) layer may couple to a tin (or gold) layer disposed on a surface of a second substrate. When melted, the gold layer and the tin layer result in an interconnect with a chemical composition having a subsequent melting temperature to reflow the bump that is higher than the initial melting temperature. For example, the chemical composition may correspond to a non-equilibrium gold-tin alloy.

Thermoelectric Mechanism and Interface Characteristics of Cyanide-Free Nanogold-Coated Silver Wire

Traditional bath-plated gold contains a cyanide complex, which is an environmental hazard. In response, this study used a green plating process to produce cyanide-free gold-coated silver (cyanide-free ACA) bonding wire that has been proven to be a feasible alternative to gold bonding wire in semiconductor packaging (Tseng et al., Journal of Electronic Materials, DOI 10.1007/s11664-015-4161-2). In this work, ACA wire annealed at 550°C was found to have stable microstructure and superior mechanical properties. Intermetallic compounds Ag_2Al and $AuAl_2$ grew from Ag-Au balls and Al pads after aging at 175°C for 500 h. After current testing, ACA wire was found to have improved electrical properties due to equiaxed grain growth. The gold nanolayer on the Ag surface increased the oxidation resistance. These results provide insights regarding the reliability of ACA wire in advanced bonding processes.

Flexible printed circuit board having gold fingers

The present invention described by Taiwanese industrial researchers (US9178295 (B1)) provides a flexible printed circuit board having gold fingers, comprising a base sheet, a metallic layer and a protective sheet. The base sheet has a plurality of voids thereon. The metallic layer is provided on the base sheet, and has at least one plated through hole. The protective sheet is provided on the base sheet and the metallic layer to expose a portion of the metallic layer and the plated through hole. The flexible printed circuit board may electrically be connected to a conductive terminal of a rigid printed circuit board with one gold finger and electrically be connected to a system with another gold finger. The plated through hole has a function of heat conduction and soldering, and the voids of the flexible printed circuit board can provide a space for overflowing solder and heat dissipation

FUEL CELL / BATTERY TECHNOLOGIES

Fuel cell system glow plug and method of forming the same

A glow plug and method of forming the same, the glow plug including a housing, a heating element extending from a first end of the housing, and a sealing element attached to the heating element and the first end of the housing. The sealing element may include an annular base and a tubular collar extending from the base. The sealing element may be attached using an ABA gold braze. The sealing element may include an austenitic nickel-chromium alloy. The glow plug may further include a landing pad configured to attach a lead wire to the heating element. The landing pad may include a collar and a lead connection extending from the collar and may be attached using the ABA gold braze. The glow plug may further include a glass sealing ring disposed between the heating element and the housing. The sealing ring may be attached using the ABA gold braze (WO2015153180 (A1)).

Understanding Moisture and Carbon Dioxide Involved Interfacial Reactions on Electrochemical Performance of Lithium–Air Batteries Catalyzed by Gold/Manganese-Dioxide

Lithium–air (Li–air) battery works essentially based on the interfacial reaction of $2Li + O_2 \leftrightarrow Li_2O_2$ on the catalyst/oxygen-gas/electrolyte triphase interface. Operation of Li–air batteries in ambient air still remains a great challenge despite the recent development, because some side reactions related to moisture (H_2O) and carbon dioxide (CO_2) will occur on the interface with the formation of some inert byproducts on the surface of the catalyst. In this work, Chinese researchers investigated the effect of H_2O and CO_2 on the electrochemical performance of Li–air batteries to evaluate the practical operation of the batteries in ambient air (Wang et al., ACS Appl. Mater. Interfaces, 2015, 7 (43), pp 23876–23884. DOI: 10.1021/acsami.5b05250). The use of a highly efficient gold/δ-manganese-dioxide (Au/δ-MnO_2) catalyst helps to understand the intrinsic mechanism of the effect. We found that H_2O has a more detrimental influence than CO_2 on the battery performance when operated in ambient air. The battery operated in simulated dry air can sustain a stable cycling up to 200 cycles at 400 mA g^{-1} with a relatively low polarization, which is comparable with that operated in pure O_2. This work provides a possible method to operate Li–air batteries in

ambient air by using optimized catalytic electrodes with a protective layer, for example a hydrophobic membrane.

PtAu Electrocatalyst for Glycerol Oxidation Reaction Using a ATR-FTIR/Single Direct Alkaline Glycerol/Air Cell In Situ Study

Different ratios of PtAu/C electrocatalysts were synthesized and assessed for their capability by glycerol electrooxidation. Electrocatalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), cyclic voltammetry (CV), chronoamperometry, and direct glycerol/air fuel cell coupled with a ATR-FTIR setup (Ottoni et al., Electrocatalysis, 2015, DOI 10.1007/s12678-015-0277-7). XRD of PtAu/C electrocatalysts showed the presence of Pt (fcc), Au (fcc), and PtAu (fcc) phases, and TEM images for PtAu/C electrocatalysts showed particle size between 5.4 and 5.8 nm. PtAu/C (50:50) presented the best result for glycerol electrooxidation by cyclic voltammetry and chronoamperommetry measurements in comparison with other electrocatalysts prepared. All PtAu/C showed better performance in comparison with Pt/C and Au/C. Moreover, the addition of gold to platinum favored glycerol by electronic effect and bifunctional mechanism. Through ATR-FTIR/direct alkaline glycerol/air cell in-situ study, it was possible to identify glycerate and tartronate as main products formed during the electrochemical glycerol oxidation

CATALYSIS

Synthesis of Au-induced structurally ordered Au-Pd-Co intermetallic core-shell nanoparticles and their use as oxygen reduction catalysts

Embodiments of the disclosure from Brookhaven scientists relate to intermetallic nanoparticles (WO2015164474 (A1)). Embodiments include nanoparticles having an intermetallic core including a first metal and a second metal. The first metal may be palladium and the second metal may be at least one of cobalt, iron, nickel, or a combination thereof. The nanoparticles may further have a shell that includes palladium and gold.

Supported gold catalyst that is thermally resistant to deactivation phenomena under operating conditions

The invention relates to a supported gold catalyst that is thermally resistant to deactivation phenomena under operating conditions. More specifically, the invention relates to a catalytic system of formulation Ce02/Au/Ti02, obtained by means of the post-synthesis modification of a gold catalyst supported on a reducible oxide, in this case TIO2. The interaction between its three components produces greater catalytic activity in the reaction used as a test (CO oxidation), but, above all, it displays greater stability during treatments in a reaction atmosphere at temperatures of the order of 1223 K. The low thermal stability of gold is currently considered to be one of the main impediments to its commercial use in processes in which it has been shown to be active. In this respect, the catalyst described is presented as a possible solution to these problems, also allowing the use of gold in catalytic applications that require severe thermal conditions (WO2015155381 (A1))

Discovery, Development and Commercialisation of Gold catalysts for Acetylene Hydrochlorination

Vinyl chloride monomer (VCM) is a major chemical intermediate for the manufacture of polyvinyl chloride (PVC) which is the third most important polymer in use today. Hydrochlorination of acetylene is a major route for the production of vinyl chloride since production of the monomer is based in regions of the world where coal is abundant. Until now mercuric chloride supported on carbon is used as the catalyst in the commercial process and this exhibits severe problems associated with catalyst lifetime and mercury loss. It has been known for over thirty years that gold is a superior catalyst but it is only now that it is being commercialised. In this perspective we discuss the use and disadvantages of the mercury catalyst and the advent of the gold catalysts for this important reaction. The nature of the active site and the possible reaction mechanism is discussed. Recent advances in the design and preparation of active gold catalysts containing ultra-low levels of gold are described by researchers in the UK in this JACS perspective article (Johnston et al., J. Am. Chem. Soc., Just Accepted Manuscript DOI: 10.1021/jacs.5b07752). In the final part a view to the future of this chemistry will be discussed as well as the possible avenues for the commercial potential of gold catalysis.

Non-mercury catalytic acetylene hydrochlorination over activated carbon-supported Au catalysts promoted by CeO_2

Gold–cerium oxide catalysts were prepared by Chinese researchers (Li et al., Catal. Sci. Technol., 2015, Advance Article DOI: 10.1039/C5CY01209K) to study the effects of cerium oxide additives on the catalytic performance of gold catalysts for acetylene hydrochlorination, using activated carbon as the support. The optimal catalytic performance is achieved over the 1Au–5CeO_2/AC catalyst with an acetylene conversion of 98.4% and a selectivity to vinyl chloride monomer (VCM) of 99.9% after 20 h on stream under the conditions of 180 °C, C_2H_2 gas hourly space velocity (GHSV) of 852 h^{-1} and HCl/C_2H_2 feed volume ratio of 1.15. It is indicated that the addition of cerium oxide can make active Au species uniformly dispersed and improve the

adsorption properties of reactants on the catalysts, but also suppress the reduction of active gold species and inhibit coke deposition on the catalyst surfaces during the reaction. Characterization was carried out using transmission electron microscopy, Raman spectroscopy, N_2 adsorption/desorption analysis, thermogravimetric analysis, temperature-programmed reduction, temperature-programmed desorption, powder X-ray diffraction, atomic absorption spectroscopy and X-ray photoelectron spectroscopy.

A Schiff base modified gold catalyst for green and efficient H_2 production from formic acid

Formic acid (FA) dehydrogenation is an atom-economic method for H_2 production, while diluted FA with extra additives is generally required in heterogeneous dehydrogenation of FA. Here, a team from Dalian report a novel Schiff base functionalized gold catalyst, which showed excellent catalytic performances for H_2 production in catalytic dehydrogenation of high-concentration FA without any additives (Liu et al., Energy Environ. Sci., 2015,8, 3204-3207. DOI: 10.1039/C5EE02506K). The record turnover frequency (TOF) was as high as 4368 h^{-1} in 10 M FA solutions, and was up to 2882 h^{-1} even in 99% FA at a mild temperature of 50 °C. According to characterization results, a synergetic mechanism for C–H activation between the protonated Schiff base and electronegative gold nanoparticles (NPs) at the interface was suggested to be responsible for its unusual catalytic activity toward H_2 production from FA.

CHEMISTRY

Gold(I) complexes with t-butyl phosphine and dialkyl dithiocarbamate ligands

Gold(I) complexes of formulae [Au{P(t-Bu)3}(S2CN(CH3)2)] (1), and [Au{P(t-Bu)3}(S2CN(C2H5)2)] (2) have been prepared by the reaction of equimolar amounts of [Au{P(t-Bu)3}(Cl)] with sodium dimethyldithiocarbamate monohydrate, and sodium diethyldithiocarbamate trihydrate respectively. Both complexes (1) and (2) are iso-structural having linear geometry. These gold(I) dithiocarbamate complexes show in vitro cytotoxic activities against A549 (human lung carcinoma), HeLa (human cervical cancer) and MCF7 (human breast cancer) cell lines (US2015266909 (A1)).

Synthesis and luminescence modulation of pyrazine-based gold(III) pincer complexes

The first examples of pyrazine-based gold(III) pincer complexes are reported by UK-based academics (Fernandez-Cestau et al., Chem. Commun., 2015,51, 16629-16632, DOI: 10.1039/C5CC07523H); their intense photoemissions can be modified by protonation, *N*-alkylation or metal ions, without the need for altering the ligand framework. Emissions shift from red (77 K) to blue (298 K) due to thermally activated delayed fluorescence (TADF).

Controlling intermolecular aurophilicity in emissive dinuclear Au(I) materials and their luminescent response to ammonia vapour

The concept that hydrogen bonding cations can reduce the coulombic repulsion inherent to anionic gold species and thereby trigger aurophilicity is realized with three new photoluminescent compounds of the form $[Q]_2[Au_2(i\text{-}mnt)_2]$ ($i\text{-}mnt = (CN)_2C{=}CS_2^{2-}$, Q = 3,5-dimethylpyrazolium, piperidinium) as described by Canadian researchers (Roberts et al., Chem. Commun., 2015,51, 14299-14302. DOI: 10.1039/C5CC05277G. These compounds illustrate unprecedented supramolecular aurophilicity between the anions, the emission of which is significantly red-shifted compared to zero-dimensional analogues, a direct result of the aurophilic network. The piperidinium salt exhibits a vapochromic/luminescent response to ammonia, inducing a change in colour of the reflectance and emission from red to yellow. These results demonstrate the ability to rationally control the formation of supramolecular metallophilic networks *via* the incorporation of hydrogen bonding cations.

COATINGS

Electrochemistry and speciation of Au^+ in a deep eutectic solvent: growth and morphology of galvanic immersion coatings

In this study German and UK scientists compare the electrochemical and structural properties of three gold salts AuCl, AuCN and $KAu(CN)_2$ in a Deep Eutectic Solvent (DES) electrolyte (Ethaline 200) in order to elucidate factors affecting the galvanic deposition of gold coatings on nickel substrates (Ballantyne et al., Phys. Chem. Chem. Phys., 2015,17, 30540-30550. DOI: 10.1039/C5CP05748E. A chemically reversible diffusion limited response was observed for AuCl, whereas AuCN and $KAu(CN)_2$ showed much more complicated, kinetically limited responses. Galvanic exchange reactions were performed on nickel substrates from DES solutions of the three gold salts; the AuCN gave a bright gold coating, the $KAu(CN)_2$ solution give a visibly thin coating, whilst the coating from AuCl was dull, friable and poorly adhesive. This behaviour was rationalised by

the differing speciation for each of these compounds, as evidenced by EXAFS methods. Analysis of EXAFS data shows that AuCl forms the chlorido-complex $[AuCl_2]^-$, AuCN forms a mixed $[AuCl(CN)]^-$ species, whereas $KAu(CN)_2$ maintains its $[Au(CN)_2]^-$ structure. The more labile Cl^- enables easier reduction of Au when compared to the tightly bound cyanide species, hence leading to slower kinetics of deposition and differing electrochemical behaviour. We conclude that metal speciation in DESs is a function of the initial metal salt and that this has a strong influence on the mechanism and rate of growth, as well as on the morphology of the metal deposit obtained. In addition, these coatings are also extremely promising from a technological perspective as Electroless Nickel Immersion Gold (ENIG) finishes in the printed circuit board (PCB) industry, where the elimination of acid in gold plating formulation could potentially lead to more reliable coatings. Consequently, these results are both significant and timely.

Scalable Microaccordion Mesh for Deformable and Stretchable Metallic Films

Elastically deformable materials can be created from rigid sheets through patterning appropriate meshes which can locally bend and flex. Here Cambridge researchers demonstrate how microaccordion patterns can be fabricated across large areas using three-beam interference lithography (Mertens et al., Phys. Rev. Applied **4**, 044006. DOI http://dx.doi.org/10.1103/PhysRevApplied.4.044006). The resulting mesh induces a large and robust elasticity within any rigid material film. Gold coating the microaccordion produces stretchable conducting films. Conductivity changes are negligible when the sample is stretched reversibly up to 30% and no major defects are introduced, in comparison to continuous sheets which quickly tear. Scaling analysis shows that our method is suited to further miniaturization and large-scale fabrication of stretchable functional films. It thus opens routes to stretchable interconnects in electronic, photonic, and sensing applications, as well as a wide variety of other deformable structures.